

## IV.B.5e Amineborane Hydrogen Storage - New Methods for Promoting Amineborane Dehydrogenation/Regeneration Reactions

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### Objectives

- Develop methods for on-demand, low temperature hydrogen release from chemical hydrides that can achieve DOE targets.
- Develop high conversion off-board methods for chemical hydride regeneration.

### Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan.

- (A) System Weight and Volume
- (B) System Cost
- (E) Charging/Discharging Rates
- (R) Regeneration Processes

### Technical Targets

- Gravimetric Density: 0.045 (2007); 0.06 (2010); 0.09 (2015) kg-H<sub>2</sub>/kg
- Volumetric Density: 0.036 (2007); 0.045 (2010); 0.081 (2015) kg-H<sub>2</sub>/L

**TABLE 1.** Progress toward DOE Targets and Comparisons of the H<sub>2</sub>-Release Properties of Penn Amineborane-Based Storage Systems

Metrics	Hydrolysis 22 °C	Thermolysis at 85 °C					
		Solid-State			Solution-State		
		22.7 wt% aq. AT (1.1 mol%Rh)	AB/LiNH <sub>2</sub> (9 mol%)	AB/LiH (17 mol%)	AB/AT(5mol%)/ PS(5mol%)	AB/PS(5mol%)/ bmimCl	AB/AT(5mol%)/ PS(5mol%)/bmimCl
Grav. density (Mat. wt%)	6.1, 4h	5.9, 3h 9.3, 15h	5.7, 3h 9.4, 15h	5.1, 1h 6.9, 3h	5.1, 3h 5.8, 6h	3.1, 1h 4.2, 3h 5.3, 6h	5.3, 1h 6.5, 3h
Vol. density (Kg-H <sub>2</sub> /L Mat.)	0.090, 4h	0.047, 3h 0.074, 15h	0.045, 3h 0.073, 15h	0.044, 1h 0.059, 3h	0.047, 3h 0.054, 6h	0.018, 1h 0.023, 3h 0.030, 6h	0.049, 1h 0.060, 3h
H <sub>2</sub> Flow Rate (g/s) per kg Material	0.0042, 4h	0.0055, 3h 0.0017, 15h	0.0053, 3h 0.0017, 15h	0.014, 1h 0.0064, 3h	0.0047, 3h 0.0027, 6h	0.0086, 1h 0.0038, 3h 0.0024, 6h	0.015, 1h 0.0060, 3h
Kg of Mat. for 0.8 mol/sec	377, 4h	295, 3h 938, 15h	304, 3h 931, 15h	114, 1h 250, 3h	342, 3h 599, 6h	186, 1h 420, 3h 670, 6h	108, 1h 267, 3h

### Accomplishments

- Demonstrated significant improvements for H<sub>2</sub>-release systems based on: ammonia triborane (AT) hydrolysis; chemically-promoted ammonia borane (AB) and AB/AT mixed-fuel thermolyses in the solid-state; and ionic-liquid based thermolyses of AB and AB/AT mixtures.
- Discovered a new H<sub>2</sub>-release system based on the chemical promotion of AB dehydropolymerization with Proton Sponge in ionic liquids, that significantly increases the rate and extent of H<sub>2</sub>-release while avoiding the formation of unwanted side products.
- Conducted detailed studies of the chemical promotion of AB H<sub>2</sub>-release by LiH, LiNH<sub>2</sub> or Proton Sponge to support an anionic dehydropolymerization mechanism.
- Demonstrated a new scheme for ammonia borane regeneration that avoids the formation of B-O intermediates.



### Introduction

The development of efficient and safe methods for hydrogen storage is a major hurdle that must be overcome to enable the use of hydrogen as an alternative energy carrier. The objectives of this project are both to develop new methods for on-demand, low temperature hydrogen release from chemical hydrides that can achieve DOE targets and to develop high-conversion off-board methods for chemical hydride regeneration.

## Approach

Because of their protonic amine-hydrogens and hydridic borane-hydrogens, amineboranes such as ammonia borane,  $\text{NH}_3\text{BH}_3$  (19.6 wt%  $\text{H}_2$ ) and ammonia triborane,  $\text{NH}_3\text{B}_3\text{H}_7$  (17.7 wt%  $\text{H}_2$ ) are unique when compared to other chemical hydrides in their potential ability to store and deliver large amounts of molecular hydrogen through dehydrogenation and hydrolysis reactions. In collaboration with the other Chemical Hydrogen Storage Center of Excellence (CHSCoE) partners, Los Alamos National Laboratory, Pacific Northwest National Laboratory, the Universities of Washington, Alabama, and Northern Arizona, Intematix, and Rohm and Haas, our approach is to develop new methods for amineborane hydrogen-release and regeneration reactions that will enable their use for chemical hydrogen storage.

## Results

### Enhanced Hydrogen Release from Ammonia Borane

Partial dehydrogenation of ammonia borane can be thermally induced in the solid-state, but to be useful for hydrogen storage, milder conditions and more controllable reactions still need to be developed. In the first years of this project, we demonstrated that chemical additives, ionic liquids, and metal catalysts could each be used to significantly increase the rate and extent of hydrogen release from ammonia borane. During the last year, significant progress was made on the development and optimization of new  $\text{H}_2$ -release systems based on: catalyzed AT hydrolysis; chemically-promoted AB, and mixed-fuel AB/AT thermolyses in the solid-state, and ionic-liquid based thermolyses of AB and AB/AT mixtures with and without chemical promotion of  $\text{H}_2$ -release. As summarized in Table 1, these studies have now provided quantitative data that allow comparisons of the  $\text{H}_2$ -release properties of seven-different types of systems that are under current study at the University of Pennsylvania. These results have clearly shown that, while improvements are still necessary, considerable progress has been made toward achieving DOE hydrogen-storage goals.

Most of our initial studies [1] of ionic liquid reactions employed the bmimCl ionic liquid, but, as summarized in Figure 1, our studies during the last year have demonstrated that both faster rates and a greatly increased extent of hydrogen release can be attained when other ionic liquids are employed.

Our studies of the role of  $\text{LiNH}_2$  and  $\text{LiH}$  in inducing  $\text{H}_2$ -release from solid-state ammonia borane demonstrated that the initial step involves deprotonation of the ammonia borane to produce the  $\text{H}_2\text{NBH}_3^-$  anion, which then induces anionic dehydropolymerization of

ammonia borane to produce a growing polyaminoborane polymer. Our most recent work has shown that strong nitrogen bases, such as Proton Sponge, can also induce  $\text{H}_2$ -release by reacting with ammonia borane to produce the  $\text{H}_2\text{NBH}_3^-$  anion and thus induce AB dehydropolymerization/ $\text{H}_2$ -release (Figure 2). Most significantly, the Proton Sponge promoted reactions avoid the formation of the unwanted  $\text{LiBH}_4$  and  $\text{NH}_3$  side-product that were observed in both the  $\text{LiNH}_2$  and  $\text{LiH}$  reactions.

### Ammonia Borane Regeneration

The efficient regeneration of ammonia borane from spent fuel  $\text{BNH}_x$  is certainly one of the most challenging problems that will have to be overcome in order to utilize ammonia borane based hydrogen storage systems. The development of a general regeneration process is

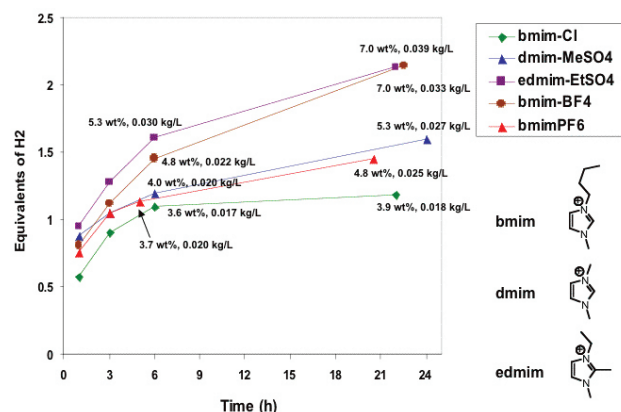


FIGURE 1. Summary of AB  $\text{H}_2$ -Release Data in Different Ionic Liquids at 85°C

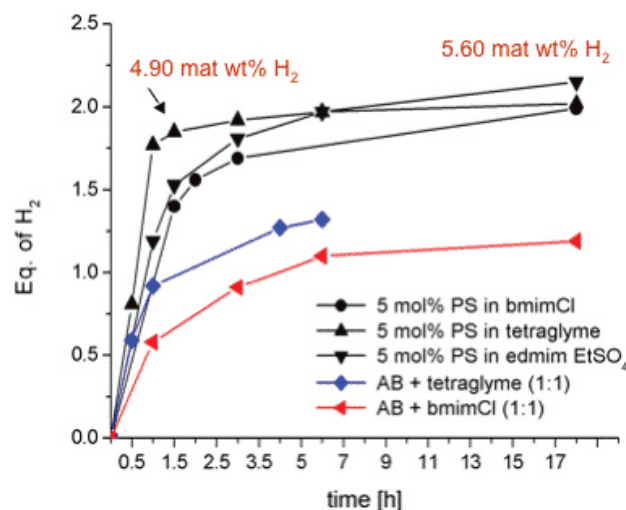


FIGURE 2. Proton Sponge Promoted AB  $\text{H}_2$ -Release in bmimCl Ionic-Liquid and Tetraglyme Solvents at 8°C

made complicated by the fact that, depending upon the conditions and extent of  $H_2$ -release, a variety of molecular, polymeric and/or solid state materials with very different chemical reactivities are formed. Thus, any viable process must both be capable of regenerating all of these spent-fuel materials and, in addition, avoid the formation of difficult to reduce intermediates (e.g. those containing boron-oxygen bonds). During the last year, we developed a new potentially general scheme for the regeneration of ammonia borane from a range of spent  $BNH_x$  fuels. As summarized in Figure 3, for a typical AB spent fuel material, the key steps in the process are: (1) digestion of the spent fuel with super acidic  $HBr/AlBr_3$  solutions; (2) coordination of the  $BBr_3$  product to diethylaniline; (3) reduction of the boron-halide bonds by triethylsilane; and (4) exchange of the diethylaniline by ammonia to regenerate  $NH_3BH_3$ . For this process to be practical, further improvements will be necessary and future work will be focused on refining and optimizing this process with the goals of achieving both complete digestion of all types of spent-fuel materials and high yields and efficient isolation of the regenerated ammonia borane.

## Conclusions and Future Directions

As discussed in the previous section, our past studies have led to the discovery and continued improvements of several promising  $H_2$ -release systems based on ammonia borane and ammonia triborane that have the potential to meet DOE targets, as well as the demonstration of a new ammonia borane regeneration process. During the next year, we plan to:

- Explore and optimize both the thermolytic  $H_2$ -release and the nitrogen-base promoted  $H_2$ -release from ammonia-borane/ammonia-triborane and related amineborane mixtures. Our preliminary

studies have provided evidence that both the rate and extent of hydrogen release is significantly greater from these mixtures, suggesting that they may ultimately prove to be the best amineborane-based fuels.

- Continue to explore and optimize the activities of new metal-catalyst and/or ionic liquids for improving the rates of thermolytic hydrogen release from ammonia borane and ammonia triborane.
- Continue to characterize the products of ammonia borane and ammonia triborane dehydrogenations under various conditions and determine their relative activity for regeneration.
- Further improve and optimize the conditions and procedures for both the digestion and reduction steps for the new ammonia borane regeneration scheme given in Figure 3.

## Special Recognitions & Awards/Patents Issued

1. Larry G. Sneddon: 2007 DOE Hydrogen Program R&D Award in Recognition of Outstanding Achievement in Storage R&D.
2. "A Promising Hydrogen-Storage Compound" Highlight in the Science and Technology Concentrates section of *Chemical and Engineering News* 2006, 84, 39.

## FY 2007 Publications/Presentations

### Publications

1. M. E. Bluhm, M. G. Bradley, and L. G. Sneddon, "Promoted Hydrogen Release from Amineborane" *Prepr. Sym., Am. Chem. Soc. Div. Fuel Chem.* **2006**, 51, 571-572.
2. C. W. Yoon and L. G. Sneddon "Ammonia Triborane: A Promising Candidate for Amineborane-Based Chemical Hydrogen Storage," *J. Am. Chem. Soc.* **2006**, 128, 13992-3.

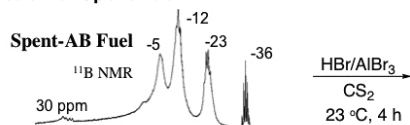
### Reports

1. Four Quarterly Reports to DOE.

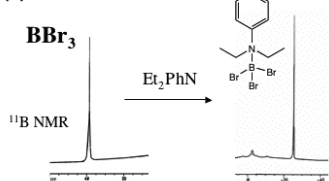
### Presentations

1. M. G. Bradley, M. E. Bluhm, and L. G. Sneddon, "Chemical Hydrogen Storage: Hydrogen Release for Ammonia Borane in Ionic Liquids" poster presentation (first place poster award) at Green Solvents for Processes conference, Friedrichshafen, October, 2006.
2. M. E. Bluhm, C. W. Yoon, D. Himmelberger, L. R. Alden, M. G. Bradley, and L. G. Sneddon, "Amineborane Chemical Hydrogen Storage," The Chinese University of Hong Kong, Hong Kong, November, 2006.
3. M. E. Bluhm, C. W. Yoon, D. Himmelberger, L. R. Alden, M. G. Bradley, and L. G. Sneddon, "Amineborane Chemical

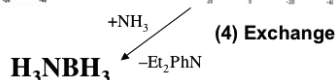
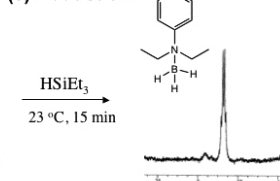
### (1) Digestion of Spent Fuel



### (2) Amine-Coordination



### (3) Reduction



**FIGURE 3.** Summary of the Penn Ammonia Borane Regeneration Scheme

Hydrogen Storage,” Korea Advanced Institute of Science and Technology, Daejeon, Korea, November, 2006.

4. M. E. Bluhm, C. W. Yoon, D. Himmelberger, L. R. Alden, M. G. Bradley, and L. G. Sneddon, “Amineborane Chemical Hydrogen Storage,” Sogang University, Seoul, South Korea, November, 2006.
5. L. G. Sneddon, M. E. Bluhm, and M. G. Bradley, “Amineborane Chemical Hydrogen Storage,” invited lecture in the symposium on Hydrogen Storage at the Materials Research Meeting, Boston, November 2006.
6. L. G. Sneddon, M. E. Bluhm, L. Alden, D. Himmelberger, and M. G. Bradley, “Amineborane Based Chemical Hydrogen Storage,” invited lecture in the Sheldon Shore Award Symposium at the National American Chemical Society Meeting, Chicago, March, 2007.
7. L. G. Sneddon, “Amineborane Based Chemical Hydrogen Storage,” DOE Tech Team Meeting, Pasco, Washington, March, 2007.
8. L. G. Sneddon, “Amineborane Based Chemical Hydrogen Storage,” DOE Hydrogen Annual Merit Review Meeting, Washington D.C., May 2007.
9. L. G. Sneddon, M. E. Bluhm, L. Alden, D. Himmelberger, M. G. Bradley, and Bill Ewing, “Amineborane Based Chemical Hydrogen Storage,” invited lecture to be presented at the Symposium on Hydrogen Storage at the Materials Science and Technology Conference, Detroit, September, 2007.
10. M. E. Bluhm, C. W. Yoon, D. Himmelberger, L. R. Alden, M. G. Bradley, and L. G. Sneddon, “Amineborane Based Chemical Hydrogen Storage,” University of Toronto, May, 2007.

## References

1. M. E. Bluhm, M. G. Bradley, R. Butterick III, U. Kusari and L. G. Sneddon, “Amineborane Based Chemical Hydrogen Storage: Enhanced Ammonia Borane Dehydrogenation in Ionic Liquids,” *J. Am. Chem. Soc.* **2006**, *128*, 7748-7749.